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UNITED STATES ARMY ENVIRONMENTAL HYGIENE AGENCY

ABERDEEN PROVING GROUND, MD 21010-5422

HAZARDOUS WASTE STUDY NO. 37-26-0115-88
EVALUATION OF THERMAL BATTERIES
FOR HAZARDOUS WASTE CHARACTERISTICS
U.S. ARMY COMMUNICATIONS - ELECTRONICS COMMAND
FORT MONMOUTH, NEW JERSEY
OCTOBER - DECEMBER 1987

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| 14. SUBJECT TERMS Thermal; batteries; environmental regulations; analysis; hazardous waste; hazardous waste characteristics; hazardous waste identification | | | |
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DEPARTMENT OF THE ARMY

U. S. ARMY ENVIRONMENTAL HYGIENE AGENCY ABERDEEN PROVING GROUND, MARYLAND 21010-6422



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REPLY TO ATTENTION OF

HSHB-ME-SH

28 March 1988

MEMORANDUM FOR: Commander, U.S. Army Materiel Command, ATTN: AMCSG, 5001 Eisenhower Avenue, Alexandria, VA 22333-0001

SUBJECT: Hazardous Waste Study No. 37-26-0115-88, Evaluation of Thermal Batteries for Hazardous Waste Characteristics, U.S. Army Communications - Electronics Command, Fort Monmouth, New Jersey, October - December 1987

EXECUTIVE SUMMARY

The purpose, major conclusions, and the major recommendations of the enclosed report follow:

- a. <u>Purpose</u>. To evaluate thermal batteries for waste disposal characteristics under the requirements of the Resource Conservation and Recovery Act (RCRA) and to provide recommendations for disposal action.
 - b. Major Conclusions.
 - (1) Unserviceable thermal batteries are a RCRA hazardous waste.
- (2) The electrochemical system used in the batteries determines which RCRA characteristic the unserviceable battery has. Some have the characteristic of EP Toxicity; others the characteristic of reactivity.
- c. Major Recommendations. To ensure regulatory compliance, the following recommendation is made: Dispose of unserviceable thermal batteries by activating them, and when cool, report them to the Defense Reutilization and Marketing Office (DRMO) for disposal as a RCRA hazardous waste. To ensure good environmental engineering practice, the following recommendation is made: Return unserviceable thermal batteries from field exercises to the host installation for disposal. Do not dispose of unserviceable thermal batteries in the field during field exercises nor discard in ordinary refuse and trash.

FOR THE COMMANDER:

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DEPARTMENT OF THE ARMY

U. S. ARMY ENVIRONMENTAL HYGIENE AGENCY ABERDEEN PROVING GROUND, MARYLAND 21010-6422



REPLY TO ATTENTION OF 28 MAR 1988

HSHB-ME-SH

HAZARDOUS WASTE STUDY NO. 37-26-0115-88
EVALUATION OF THERMAL BATTERIES
FOR HAZARDOUS WASTE CHARACTERISTICS
U.S. ARMY COMMUNICATIONS - ELECTRONICS COMMAND
FORT MONMOUTH, NEW JERSEY
OCTOBER - DECEMBER 1987

- 1. AUTHORITY. FONECON between MAJ Cabellon, HQAMC, and Mr. David Guzewich, USAEHA, 20 August 1986, subject: Thermal Batteries.
- 2. PURPOSE. To evaluate thermal batteries for waste disposal characteristics under the requirements of the Resource Conservation and Recovery Act (RCRA) and to provide recommendations for disposal action.
- 3. SCOPE. The U.S. Environmental Protection Agency (EPA) states in 40 CFR 262.11(c) two alternative methods for determining if a waste should be classified as hazardous. Those methods are:
- a. Testing the waste according to the methods set forth in Subpart C of 40 CFR 261, or according to an equivalent method approved by the EPA Administrator under 40 CFR 260.21.
- b. Applying knowledge of the hazard characteristic of the waste in light of the materials or the processes used. The evaluation described in this report was conducted by applying knowledge from literature sources and from personnel who know and work with thermal batteries. The U.S. Army Environmental Hygiene Agency (USAEHA) personnel did not perform analytical testing of the batteries.

4. BACKGROUND.

- a. Thermal (heat-activated) batteries have been used for many years in various weapons and ordnance items. The batteries use inorganic salt electrolytes that are nonconductive solids at ambient temperatures and an integral pyrotechnic mixture sized to generate enough heat to melt the electrolyte (reference 13).
- b. The batteries are activated by any one of three kinds of signals to a built-in squib or primer: either an electrical, mechanical, or inertial signal. The squib or primer ignites the pyrotechnic which melts the electrolyte and permits the battery to deliver high power for relatively short durations (references 13 and 16).
- c. Thermal batteries that have been used in detonated ordnance items are not an issue in this evaluation. When the ordnance item has exploded, there is no collectible waste. After the explosion of the ordnance item, the residues from the battery are a moot point from a regulatory standpoint.

5. DISCUSSION.

a. Chemistry of Thermal Batteries.

- (1) Approximately 10 percent of the weight of a thermal battery is pyrotechnic mix. It is used to raise the temperature enough to liquefy the electrolytic salts in the cells and produce power flow in a functional battery. The pyrotechnic is completely used up when the battery is activated (reference 16). When the battery cools, the cell contents reharden and power flow stops. Thermal batteries cannot be reactivated to produce power after they have been fired and subsequent cooling has occurred.
- chemistry. Lithium chloride is part of the electrolyte. Byproducts of the reaction include calcium chloride, a chromium trioxide-calcium oxide mixture, and lithium oxide. Various chemical side reactions may occur. Zirconium-barium chromate heat paper is used as a heat source. Batteries with heat paper start out with 10 to 15 percent of total battery weight as barium chromate. The self-discharge reaction of calcium with calcium chromate is exothermic. Temperatures within cells range from 485- to near 600-degrees centigrade. This data is based on thermal couple testing. Electrical power is produced during the time when the internal temperature of the cells is hot. Power production ceases when the cells cool and the molten internal chemistry returns to an amorphous solid state.
- (a) After power has been produced, thermal batteries with this chemistry have 5- to 7-percent barium chromate (heat paper types) and 5- to 7-percent chromic oxide remaining. Batteries that use heat pellets start out with 5- to 7-percent chromate and do not change with burning (reference 15).
- (b) It is reasonable to believe and it is our judgement that if the battery contents were subjected to the test for the RCRA Characteristic of extraction procedure (EP) Toxicity (40 CFR 261.24), the analytical results would probably equal or exceed the maximum concentration of 5.0 milligrams per liter for chromium. This evaluation has been informally coordinated with the EPA (reference 18).
- (c) The exclusion regarding wastes that are trivalent chromium [40 CFR 261.4(b)(6)] is not valid or appropriate to wastes from thermal batteries with the calcium/calcium chromate chemistry. The battery chemistry is predominantly one involving hexavalent chromium. The exclusion is not applicable because of the stoichiometric absence of trivalent chromium and because the waste is not generated from an industrial process which uses trivalent chromium exclusively.
- (d) These calcium/calcium chromate batteries should, therefore be managed as RCRA hazardous wastes because they exhibit the Characteristic of EP Toxicity for chromium. They have the EPA Hazardous Waste Number of D007.

- (e) The Item Manager for these batteries should contract with an appropriate laboratory to run tests to verify, through analysis, the determination made in this evaluation [40 CFR 262.11(c)(1)]. At present, the test for the characteristic of EP Toxicity (40 CFR 261.24) should be conducted to verify the determination. When the EPA makes the proposed Toxicity Characteristic Leaching Procedure (TCLP) final as the replacement for the EP Toxicity test, the Item Manager should retest the batteries using the TCLP (reference 9).
- (3) Some thermal batteries use a lithium/iron disulfide electro-chemistry. These batteries use a lithium metal anode and are reported to give improved performance. A lithium chloride-potassium chloride electrolyte is used. When activated, the cells reach temperatures which permit melting of the the contents, just as with the calcium/calcium chromate thermal batteries (references 13 and 16).
- (a) After power has been produced, thermal batteries with this electrochemistry have lithium sulfide and iron sulfide in the cells. There may also be a small amount of unreacted lithium metal in the cells (reference 16).
- (b) As was the case with lithium-sulfur dioxide batteries, the thermal batteries with the lithium chemistry described above require management as a hazardous waste (references 8, 14, and 18). In addition, these "fired" or spent thermal cells constitute a sulfide-bearing waste. There is no way to inactivate or further react away any remaining lithium metal in a cooled down battery (reference 16).
- (c) These spent batteries should, therefore, be managed as RCRA hazardous wastes because they exhibit the Characteristic of Reactivity. They have the EPA Hazardous Waste Number of DOO3.
- (d) We do not know of any reasonable tests to verify, through analysis, the determination made in this evaluation. Because spent cells contain a sulfide-bearing waste and because there is the probability of some unreacted lithium metal left in the cells, laboratory testing for the relevant properties of the reactivity characteristic is considered unnecessary.

b. Configuration.

- (1) Thermal batteries are made in a wide variety of sizes and shapes to meet specific applications. Most thermal batteries have several cells. The entire battery is hermetically sealed in a steel can (references 13 and 16).
- (2) Some of the batteries with the calcium/calcium chromate electrochemistry contain asbestos. It is in the form of a tight, nonfriable paper. In one laboratory, monitoring for airborne asbestos was performed extensively, and no asbestos fibers were detected in the breathing zones of

workers (reference 16). Asbestos in thermal batteries does not constitute a disposal problem. Its presence does not add additional disposal considerations.

- (3) The constituents in thermal batteries are not proprietary. Each of the three companies that make these batteries has a part number for each type made. Obtaining the part number and any national stock number (NSN) relating to it was outside the scope of this evaluation.
- (4) Item Managers for thermal batteries should contact the manufacturers and obtain from them a list that shows the part number, corresponding NSN, and the type of chemistry used. This information, when published, will help the regulated community of hazardous waste generators distinguish one chemistry from another for the purpose of properly managing the wastes.

c. <u>Management</u>.

- (1) Thermal batteries are to be managed as a RCRA hazardous waste. The quantity generated counts toward the calculable quantity for each generator (i.e., military installation with an EPA Identification number).
- (2) Unserviceable thermal batteries should be "fired" or activated to generate their electricity, allowed to cool, and then be collected and reported to the servicing Defense Reutilization and Marketing Office (DRMO) for disposal. This is stated in section 10c, chapter VI of DOD 4160.21-M (reference 1). Generating activities should coordinate the turn-in to the DRMO with the installation environmental coordinator.
- (3) If unserviceable thermal batteries, when fired, do not heat up or if it cannot be determined whether or not the battery had been fired, the following alternative procedures are suggested:
- (a) Take the batteries in question to the open burning grounds at the installation, and thermally treat them in such a way that the pyrotechnic in the battery will ignite and burn. Perform this treatment in pans to prevent any ground contamination and to facilitate collection of the residue. Allow to cool and turn in residues as described previously in paragraph 5c(2). This procedure is thermal treatment of a hazardous waste (40 CFR 260.10, 40 CFR 270.2, and 40 CFR 270.10) and requires a permit. Coordinate with and obtain concurrence from the environmental coordinator for the installation or facility before conducting this procedure.
- (b) Contact the Explosive Ordnance Disposal (EOD) team to ascertain whether it is appropriate for them to conduct the procedure described above in paragraph 5c(3)(a).
- (c) If the thermal treatment cannot be performed at the installation or facility, contract with a permitted hazardous waste transporter and treatment/storage/disposal facility to dispose of the thermal batteries for which the pyrotechnic status is questionable. The DRMO should be able to assist in finding and contracting with an appropriate firm.

(4) Any generator that does not or cannot use the services of the DRMO should manifest the spent batteries to a permitted hazardous waste treatment/storage/disposal facility using a licensed hazardous waste transporter (40 CFR 262.20).

d. Field Disposal.

- (1) Unusable or spent thermal batteries must not be disposed of in the field by military units on field training exercises. Batteries should be returned to the host or home installation for disposal action through established hazardous materials/hazardous waste management procedures.
- (2) Thermal batteries should not be disposed of as ordinary solid waste or refuse.

6. CONCLUSIONS.

- a. Thermal batteries are a RCRA hazardous waste. This determination pertains to both discharged (i.e., fired) or undischarged batteries that cannot be fired but that require disposal action.
- b. Thermal batteries with the calcium/calcium chromate electrochemical system exhibit the RCRA Characteristic of EP Toxicity and have the EPA Hazardous Waste Number of DOO7.
- c. Thermal batteries with the lithium/iron disulfide electrochemistry exhibit the RCRA Characteristic of reactivity and have the EPA Hazardous Waste Number of DOO3.

7. RECOMMENDATIONS.

- a. To ensure regulatory compliance, the following recommendations are made:
- (1) Dispose of unserviceable thermal batteries by activating them and, after the proper cool-down period, reporting them to the servicing DRMO for disposal as a hazardous waste [40 CFR 262; DOD 4160.21-M, chapter VI, paragraph 10 c; and DPDS-M 6050.1, Section V, Chapter 6, paragraph D.2.h].
- (2) Ascertain the most appropriate method for thermally treating batteries for which it cannot be determined whether or not the pyrotechnic mix has been burned, as described in paragraph 5c(3) of this report (40 CFR 270.10).
- (a) Manage thermal batteries with the calcium/calcium chromate electrochemistry as EP toxic hazardous wastes [40 CFR 261.24(b)].
- (b) Manage thermal batteries with the lithium/iron disulfide electrochemistry as reactive hazardous wastes [40 CFR 261.23(b)].

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- (3) Confirm the hazardous waste determination by analytical testing, particularly with regard to the thermal batteries having the calcium/calcium chromate electrochemistry [40 CFR 262.11(c)(1)]. Reconfirm the determination when the proposed TCLP for testing wastes is promulgated by the EPA.
- b. To ensure adherence to good environmental engineering practices, the following recommendations are made:
- (1) Return all used or unserviceable thermal batteries from field training exercises to the home installation for disposal action. Do not dispose of the batteries in the field during field exercises.
- (2) Do not dispose of thermal batteries as ordinary solid waste (i.e., refuse).
- (3) Have Item Managers obtain information from manufacturers of thermal batteries regarding the NSN's and part numbers of their batteries having the calcium/calcium chromate electrochemistry and those having the lithium/iron disulfide electrochemistry. Publish that information along with safety considerations and packaging, labeling, and marking requirements in the U.S. Army Communications Electronics Command Battery Disposition/-Disposal Handbook.
- 8. TECHNICAL ASSISTANCE. Informal technical advice and/or consultation regarding this report may be obtained by contacting the Chief, Waste Disposal Engineering Division, this Agency (AUTOVON 584-3651, Commercial 301-671-3651). Requests for services should be directed through appropriate command channels of the requesting activity to Commander, U.S. Army Environmental Hygiene Agency, ATTN: HSHB-ME-SH, Aberdeen Proving Ground, MD 21010-5422, with an information copy furnished to the Commander, U.S. Army Health Services Command, ATTN: HSCL-P, Fort Sam Houston, TX 78234-6000.
- 9. REFERENCES. See the Appendix for a list of references.

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Waste Disposal Engineering Division

APPROVED:

Program Manager

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APPENDIX

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- 16. FONECON between Dr. Jeffrey Nelson, Harry Diamond Laboratories and Mr. Michael Diem, USAEHA, 14 December 1987, subject: Chemistry, Characteristics, and Disposal of Thermal Batteries.
- 17. FONECON between Mr. John Feustle, Harry Diamond Laboratories and Mr. Michael Diem, USAEHA, 14 and 16 December 1987, subject: Disposal of Thermal Batteries.
- 18. FONECON between RCRA Superfund Hotline, Washington, DC, and Mr. Michael Diem, USAEHA, 15 December 1987, subject: RCRA Considerations in the Disposal of Thermal Batteries.